

Charge-transfer adducts between donors containing chalcogens (S and Se) and di-iodine: solution studies

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Abstract

The solution equilibria related to the 1:1 charge-transfer adduct formation between molecular iodine and several substrates containing sulfur and selenium donor atoms have been reviewed and the corresponding thermodynamic parameters (K and ΔH°) reported for a series of thiones, selones, sulfides and selenides. A survey of the several calculation Although the methods and techniques employed are very different, some correlations between the thermodynamic parameters and other experimental data, such as $\nu(\text{I}-\text{I})$ Raman methods, based on UV–vis and in some cases ^{13}C -NMR spectroscopies, is also reported.

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frequencies or UPS-binding energies, are reviewed and general conclusions drawn. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The great interest in the reaction of di-iodine with compounds containing sulfur and/or selenium donor atoms (D) [1] is continuously increasing thanks to the biological and pharmaceutical applications [2–8] and to the importance of chalcogen-based new materials in electrical properties [9]. While a large variety of different products can be obtained in the solid state (such as simple charge-transfer adducts [10–13] and adducts having soft–soft interactions with additional di-iodine molecules [14], hypervalent chalcogen compounds [11,12,15,16] oxidation products of the donor molecules to dications containing a Se–Se bridge [17], dichalcogen hypervalent two-coordinated complexes of iodine (I) [12,18] and mixed-valence compounds [19] together with polyiodides of different structural complexity [20]), only 1:1 CT-complexes are generally found in solution, according to the following equilibrium:



It is well-known that in these complexes, the interaction between a lone pair of the donor atom and I_2 leads to an increase in the I–I bond distance. The simplified MO description showing the interaction between the σ^* antibonding LUMO orbital of I_2 and the HOMO orbital of the donor accounts for this lengthening, since mixing of these orbitals allows the transfer of a fractional negative charge from the donor to the σ^* orbital [21]. The greater the donor/acceptor interaction, the greater the amount of charge transferred from the donor to the σ^* antibonding orbital of I_2 , and the greater the I–I bond lengthening. The formation of an adduct of the charge-transfer type can easily be noticed in solution thanks to a new strong band (the CT band) in the UV–vis spectra of donor/acceptor mixtures. Thanks to this CT band, the experimental UV–vis spectra of different mixtures of the donor and the acceptor can be used to evaluate the formation constants (K) and thermodynamic parameters [22] of the equilibrium (1). In some cases, the strength of the donor/di-iodine interaction was evaluated either from the changes in the ^{13}C -NMR chemical shifts of the donor induced by I_2 , or from the lowering of the $\nu(\text{I}–\text{I})$ stretching vibration of I_2 due to its interaction with the donor, as measured by FT-Raman spectroscopy.

All the substrates reviewed are collected in Fig. 1. The paper is organized in six sections. The first section is a summary of the methods used for the simultaneous determination of K and ε (molar extinction coefficient of DI_2). The following four sections present the results obtained with thiones, selones, sulfides and selenides as donors, respectively. The final section is dedicated to few general conclusions.

2. Data treatment

The thermodynamic parameters of the equilibrium (1) have been determined by several chemometric methods based on UV–vis and/or NMR spectroscopies. For each reviewed compound, the method used by the authors for the determination of K and ε is reported in the tables. Several solutions with different donor/di-iodine concentration ratios have been examined and the changes in some significant

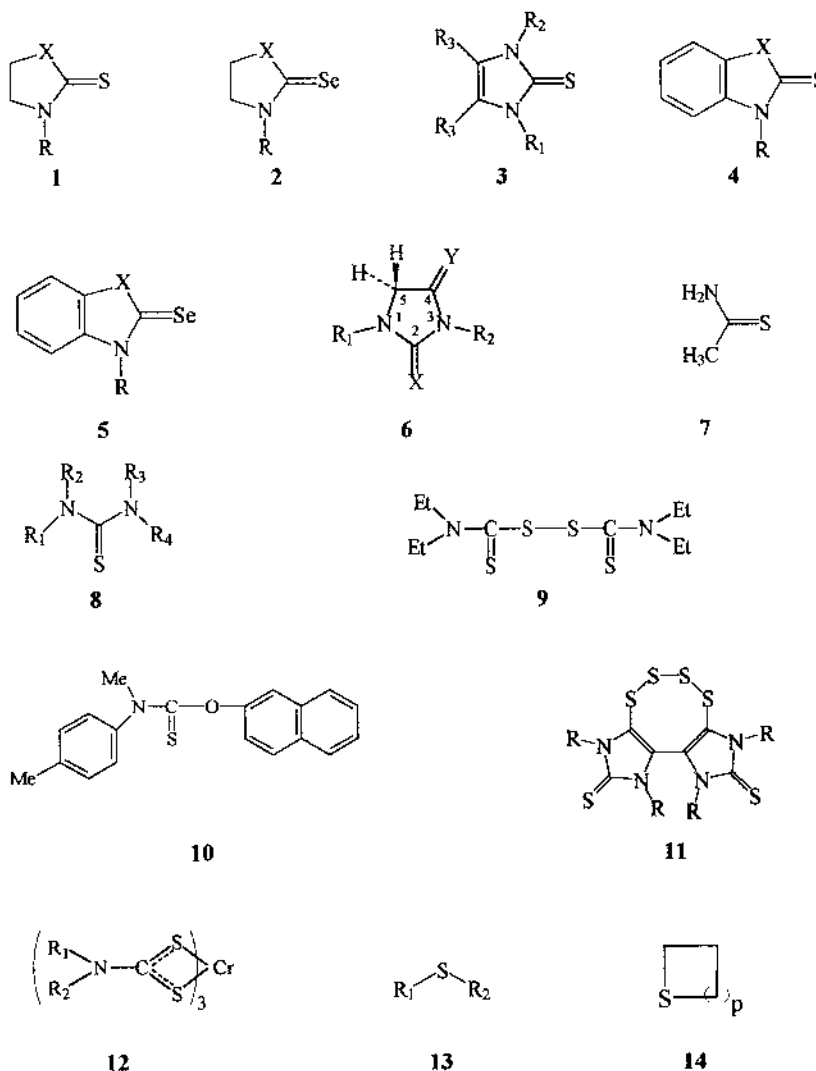


Fig. 1. Reviewed sulfur and selenium containing donors. For the substituents of the different classes of molecules see the appropriate table.

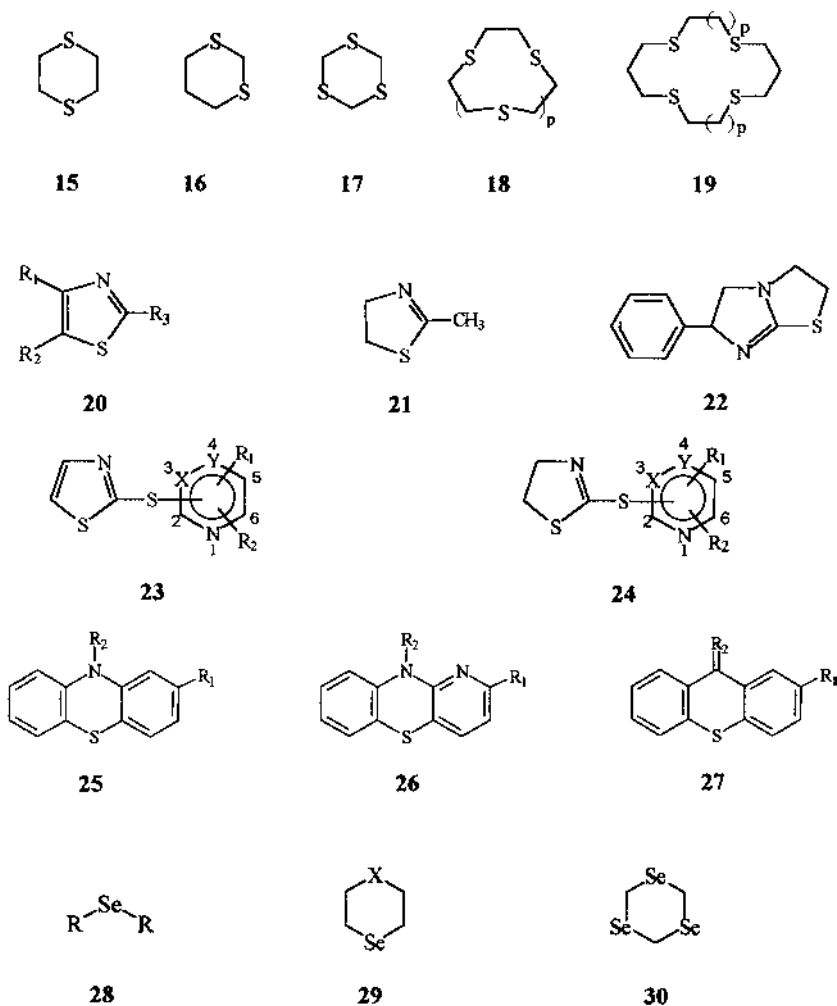


Fig. 1. (Continued)

parameters (such as the positions of the blue shifted di-iodine bands and the CT band, or the chemical shifts of nuclei in the donor molecules) have been followed.

The formation constant K is expressed by:

$$K = \frac{[DI_2]}{[D][I_2]} = \frac{[DI_2]}{([D]^\circ - [DI_2])([I_2]^\circ - [DI_2])} \quad (2)$$

where $[D]$, $[I_2]$ and $[DI_2]$ represent the equilibrium concentrations of the donor, di-iodine and their 1:1 adduct, respectively, while $[D]^\circ$ and $[I_2]^\circ$ are the analytical concentrations of the reactants. Expression (2) can be re-arranged as:

$$\frac{[I_2]^\circ}{[DI_2]} = \frac{1}{K[D]^\circ} + \frac{[I_2]^\circ}{[D]^\circ} + 1 - \frac{[DI_2]}{[D]^\circ} \quad (3)$$

If DI_2 is the only absorbing species at the examined wavelength, assuming a unit path length, according to the Lambert–Beer law, the absorbance A is expressed as:

$$A = \varepsilon \cdot [DI_2] \quad (4)$$

where ε is the molar absorptivity of the complex. Eq. (3) then becomes:

$$\frac{[I_2]^\circ}{A} = \frac{1}{K\varepsilon[D]^\circ} + \frac{[I_2]^\circ}{\varepsilon[D]^\circ} + \frac{1}{\varepsilon} - \frac{[DI_2]}{\varepsilon[D]^\circ} \quad (5)$$

For weak adducts, when $[D]^\circ \gg [I_2]^\circ$, Eq. (5) can be simplified to:

$$\frac{[I_2]^\circ}{A} = \frac{1}{K\varepsilon[D]^\circ} + \frac{[I_2]^\circ}{\varepsilon[D]^\circ} + \frac{1}{\varepsilon} \quad (6)$$

which is known as the Benesi–Hildebrand equation [23]. Therefore, the values of K and ε can be obtained graphically by measuring A for a series of analytical concentrations of the reagents (Method 1).

The expression (5) is often used in its Scott modification [24]:

$$\frac{[I_2][D]^\circ}{A} = \left([I_2]^\circ + [D]^\circ - \frac{A}{\varepsilon} \right) \frac{1}{\varepsilon} + \frac{1}{K \cdot \varepsilon} \quad (7)$$

which can be simplified to:

$$\frac{[I_2][D]^\circ}{A} = \frac{[D]^\circ}{\varepsilon} + \frac{1}{K \cdot \varepsilon} \quad (8)$$

if $[D]^\circ$ is much higher than $[I_2]^\circ$. Starting from initial guesses, Eq. (8) is iteratively applied up to consistent values of the two unknowns K and ε (Method 2) [25,26].

If one or both reacting species absorb in the examined region of the spectrum, other equations are used, such as the Ketelaar equation [27] (Method 3), or the Rose–Drago equation [28] (Method 4) from which the Benesi–Hildebrand equation is obtained with suitable simplifications. From the K values at different temperatures, ΔH° and ΔS° are directly obtained using the van't Hoff equation. The previous methods have been used extensively in the past to determine the K values of equilibrium (1) and several data reported in this review have been calculated by these equations. It should be noted that they are valid as long as the 1:1 adduct is the only formed species. This condition has been verified by checking for well-defined isosbestic points, Job's plots, verifying the linearity of Eq. (6), or in some cases [3,29] by the numerical method of Liptay [30].

However, it was only in the early 1980s that the problem of the experimental design was discussed on the basis of chemometrics. A matricial approach [31] to the problem allowed the development of computer programs [32,33] capable of determining simultaneously ε and K by solving the equations as a function of a new variable:

$$A = \frac{1}{K \sqrt{([D]^\circ + [I_2]^\circ + K^{-1})^2 - 4[D]^\circ[I_2]^\circ}} \quad (9)$$

The problem was solved (Method 5) with the well-known Gauss–Newton method [34], minimizing the function:

$$\chi^2 = \sum_i^M \sum_j^Q \{A_{ij} - \varepsilon_j [\text{DI}_2]_i^{\text{calc}}(K)\}^2 \quad (10)$$

where A_{ij} is the j th wavelength at the i th concentration ratio, Q is the number of wavelengths, M is the number of solutions, ε_j is the absorptivity at the j th wavelength and $[\text{DI}_2]_i^{\text{calc}}$ is the calculated concentration of the adduct, which again is a function of K . The error matrix can be expressed in terms of A :

$$S_K^2 = \frac{K^2 \sum \frac{(A_{\text{exp}} - A_{\text{calc}})^2}{N-2}}{\sum (A - \bar{A})^2}; \quad S_\varepsilon^2 = \sum \frac{(A_{\text{exp}} - A_{\text{calc}})^2}{N-2} \cdot \varepsilon^2 \cdot \frac{\bar{A}^2}{\sum (A - \bar{A})^2 \bar{A}^2} \quad (11)$$

where S_K and S_ε are the errors on K and ε , A_{exp} and A_{calc} are the experimental and calculated absorbances and N is the number of data points. Eq. (11) gives the criterion for the choice of the experimental points in order to reduce the errors on K and ε : $(A - \bar{A})$ must be as large as possible. The goodness-of-fit on K and ε depends on the possibility to prepare experimental solutions with A far from $\bar{A}$, i.e. with saturation fractions¹ of the complex as close to 0 and 1 as possible. The reliability of the K values can be shown graphically by reporting the sum of the squared deviation χ^2 as a function of K [35,36].

Thanks to the fast evolution in computing, a more complex program (Keps11) was developed by Crisponi et al. [37]. As the calculated absorbance has a linear dependence on ε , and a non-linear dependence on K , starting from initial estimates, Keps11 alternates a linear least-square cycle to determine ε and a non-linear Gauss–Newton cycle to calculate K , iteratively repeating the procedure until χ^2 is minimized with respect to the two variables (Method 6). During the same years, other programs were developed for equilibria involving the formation of adducts higher than 1:1 [38]. In the field of CT adducts with molecular di-iodine, the first program SUPERQUAD [39,40] (deriving from the MINQUAD program [41]) was followed by the HYPERQUAD system of programs (Method 7) [42]. These programs work on a whole set of equilibria optimizing simultaneously both the ε values of the various species and the global constants, β , with iterative Gauss–Newton or Newton–Raphson least-squares cycles after imposing a model. The same authors have recently developed a new program, POWELSPEC, which allows the refinement of the standard enthalpy and entropy changes from a set of absorbance data at different temperatures [43] (Method 8). All these programs have found better application when adducts higher than 1:1 were hypothesized or found [15], and have sometimes been associated with curve decomposition programs such as Specpeak [44], which allow the absorbance of the absorbing species be obtained. In some cases, in order to avoid higher adducts, and therefore to determine a more reliable value for the first adduct

¹ The saturation fraction of the complex is defined as the ratio between the complex concentration and that of the limiting reagent.

formation constant, suitable experimental conditions have been chosen, with the donor concentration always in excess of the di-iodine concentration [14,43,45,46]. Because of the high correlation sometimes encountered between ε and K values, the enthalpies have been calculated averaging the slopes of the lines obtained by plotting $\ln(K \cdot \varepsilon)$ vs. $1/T$ [14]:

$$\Delta H^\circ = \frac{\sum_i \Delta H_i^\circ / \sigma_i}{\sum_i 1/\sigma_i}; \quad \sigma = \sqrt{\frac{(L-1) \sum_i \sigma_i^2}{L \cdot Q(L \cdot Q - 1)}} \quad (12)$$

where L and Q are the numbers of the different temperatures and wavelengths, respectively. In some cases, equilibrium (1) has also been studied by ^{13}C -NMR, following the changes of the chemical shifts of the carbons with increasing amounts of di-iodine (Method 9) [13,47]. If δ_D^0 is the chemical shift of the examined carbon atom in the free donor and $\delta_{\text{DI}_2}^0$ that of the same carbon atom in the 1:1 adduct, the observed chemical shift δ is a weighted average between the two signals. Under the condition that the exchange time is fast compared with the NMR time scale, δ is expressed by:

$$\delta = \delta_D^0 \frac{[\text{D}]}{[\text{D}]^\circ} + \delta_{\text{DI}_2}^0 \frac{[\text{DI}_2]}{[\text{D}]^\circ} \quad (13)$$

Considering a set of solutions and introducing the mass balance, Eq. (13) becomes:

$$(\delta_i - \delta_D^0)[\text{D}]_i^\circ = [\text{DI}_2]_i (\delta_{\text{DI}_2}^0 - \delta_D^0) \quad (14)$$

δ_i being the observed chemical shift in the i th solution having $[\text{D}]_i^\circ$ and $[\text{I}_2]_i^\circ$ analytical concentrations. Introducing the expression for K , Eq. (14) becomes:

$$\begin{aligned} \Delta\delta_i &= \delta_i - \delta_D^0 \\ &= \frac{[\text{D}]_i^\circ + [\text{I}_2]_i^\circ + K^{-1} - \sqrt{([\text{D}]_i^\circ + [\text{I}_2]_i^\circ + K^{-1})^2 - 4[\text{D}]_i^\circ [\text{I}_2]_i^\circ}}{2[\text{D}]_i^\circ} (\delta_{\text{DI}_2}^0 - \delta_D^0) \end{aligned} \quad (15)$$

where $\Delta\delta_i$ depends linearly on $\delta_{\text{DI}_2}^0$ and non-linearly on K . Using Eq. (15) and introducing the K value calculated from spectrophotometric data, it is possible to evaluate $\delta_{\text{DI}_2}^0$ and consequently to determine the concentration of the adduct for each solution [13,47]. The expression can also be solved with Keps11 [48], obtaining $\delta_{\text{DI}_2}^0$ and a K value completely independent of spectrophotometric data [49]. According to Eq. (14), the straight line reporting $(\delta - \delta_D^0)$ vs. the calculated $[\text{DI}_2]$ confirms the formation of the 1:1 adduct in the explored range of concentrations.

3. Thiones

The formation constants (K) at 25°C together with ΔH° values of the reviewed thiones **1**, **3**, **4**, **6–12** for reaction (1) are reported in Tables 1–6. For **1**, K values strongly depend on the nature of the substituent X in the ring, according to the variation of the charge density on the sulfur donor atom (Table 1) [50–52]. The

Table 1

Formation constants K (25°C) and enthalpies ΔH° for 1:1 adducts between di-iodine and several thiones (**1**) and selones (**2**)^a

	X	R	Solvent	1			2		
				K^b (dm ³ mol ^{−1})	$-\Delta H^\circ$ (kJ mol ^{−1})	Ref.	K^b (dm ³ mol ^{−1})	$-\Delta H^\circ$ (kJ mol ^{−1})	Ref.
a	CH ₂	H	CH ₂ Cl ₂	$4.0(2) \times 10^4$	48(2)	[50]	–	–	–
b	NH	H	CH ₂ Cl ₂	$5.06(3) \times 10^4$	46(1)	[52]	1.34×10^6	32	[65]
c	NH	Me	CH ₂ Cl ₂	$4.95(5) \times 10^4$	59(2)	[52]	2.59×10^6	26	[65]
			CCl ₄	$1.45(5) \times 10^4$	45(1)	[52]	3.58×10^5	33	[65]
d	NH	Et	CH ₂ Cl ₂	$8.27(17) \times 10^4$	62(3)	[52]	1.37×10^6	50	[65]
			CCl ₄	$3.31(4) \times 10^4$	46(2)	[52]	3.15×10^5	43	[65]
e	NMe	Me	CH ₂ Cl ₂	$8.1(3) \times 10^3$	38(3)	[52]	3.44×10^5	33	[65]
			CCl ₄	$3.0(1) \times 10^3$	34(1)	[52]	3.97×10^5	44	[65]
f	NEt	Et	CH ₂ Cl ₂	$8.5(2) \times 10^3$	37(1)	[52]	6.20×10^5	51	[65]
			CCl ₄	$3.1(1) \times 10^3$	33(2)	[52]	3.68×10^5	46	[65]
g	O	H	CH ₂ Cl ₂	$7.0(1) \times 10^2$	35(1)	[50]	–	–	–
h	O	Me	CH ₂ Cl ₂	–	–	–	2.17×10^4	40	[36]
i	S	H	CH ₂ Cl ₂	2.88×10^3	53(4)	[50]	$4.2(9) \times 10^{4c}$	–	[65]
			CCl ₄	1.88×10^3	46(2)	[50]	–	–	–
			CCl ₄	1.82×10^3	45(6)	[29]	–	–	–
j	S	Me	CH ₂ Cl ₂	1.15×10^3	43(1)	[50]	2.37×10^4	40	[65]
			CCl ₄	$1.8(1) \times 10^2$	42(2)	[50]	–	–	–

^a Calculated according to Methods 2 and 5, respectively (see Section 2).^b Interpolated K values at 25°C are reported without standard deviations.^c $t = 17^\circ\text{C}$.

presence of a NH group in the donor molecule generally gives more stable adducts than in the case of NR (R = alkyl; compare, for example, the stability constants of **1c** and **1d** with those of **1e** and **1f**). This difference has been explained in terms of the intramolecular H-bond between NH and di-iodine in the adduct [50,52]. This is also the reason why in the solid state, the di-iodine molecule lies roughly in the same plane of the molecule [13]. The formation constants of the variously substituted imidazoline-2-thiones (**3**) locate them among the strongest donors towards di-iodine (Table 2) [2,43,53,55]. In **4**, the presence of a condensed benzene ring generally lowers the donor properties of the thioxo group (Table 3) [36].

A dependence of the adduct stability on solvent polarity has been found and discussed in terms of Mulliken's CT theory [26,52,56,57]. Considering the series of the hydantoin derivatives (Table 4) [58–61] containing only exocyclic oxygen or sulfur atoms (**6a–l**), molecular iodine always binds the sulfur atoms forming 1:1 adducts only. The comparison of the couples **6a/6e** and **6b/6f** shows the different donor abilities of the sulfur atoms in the two positions of the ring: C(2)=S binds di-iodine more strongly than C(4)=S, and this is in good agreement with the higher charge density on the sulfur atom bonded to C(2) [58]. As a consequence, also in the case where two thioxo groups are present in the donor (**6g–j**), molecular iodine always interacts with the sulfur bound to C(2) [58]. In these cases, the exclusive formation of the 1:1 adduct involving the C(2)=S sulfur was independently proved

Table 2

Formation constants K (25°C) and enthalpies ΔH° calculated according to the Method 2 (see Section 2) for 1:1 adducts between di-iodine and imidazoline-2-thione derivatives^a (**3**)

	R ₁	R ₂	R ₃	Solvent	K (dm ³ mol ⁻¹)	$-\Delta H^\circ$ (kJ mol ⁻¹)	Ref.
3a	H	H	H	CH ₂ Cl ₂	$4.95(2) \times 10^4$	38	[53]
b	Me	H	H	CH ₂ Cl ₂	$8.47(4) \times 10^4$	40	[53]
				CCl ₄	$1.67(6) \times 10^4$	36(2)	[53]
				CCl ₄	1.84×10^4	36	[2] ^b
c	Me	Me	H	CH ₂ Cl ₂	$1.07(1) \times 10^5$	41	[53]
				CCl ₄	$2.71(3) \times 10^4$	40	[53]
d	H	H	Me	CH ₂ Cl ₂	$7.35(8) \times 10^4$	40	[53]
e	Me	H	Me	CH ₂ Cl ₂	$1.12(1) \times 10^5$	41	[53]
f	H	H	Ph	CH ₂ Cl ₂	$1.26(5) \times 10^4$	34	[53]
g ^c	Me	-(CH ₂) ₂ -	H	CHCl ₃	6.309×10^3	36.4(4)	[43]
h ^c	Me	-(CH ₂) ₂ -	H	CHCl ₃	2.2387×10^4	43.4(3)	[43]

^a Buxeraud et al. [55] have recently studied 3-mercapto-1,2,4-triazole and 3-mercapto-1-methyl-1,2,4-triazole for their antithyroid activity. They report the formation constants of the adducts with di-iodine (1778 and 203 dm³ mol⁻¹ for the two compounds, respectively), but no specifications are given on the solvent, temperature, or calculation methods.

^b This molecule was reported as a thiol, but no evidence for the presence of the SH group is found in solution.

^c For **3g** and **3h**, K and ΔH° values related to the 1:2 adduct formation have been calculated according to Method 8 in Section 2. **3g**: $K_2 = 398$ dm³ mol⁻¹ $-\Delta H_2^\circ = 41.4(8)$ kJ mol⁻¹. **3h**: $K_2 = 2511$ dm³ mol⁻¹ $-\Delta H_2^\circ = 52.7(4)$ kJ mol⁻¹.

Table 3

Formation constants K (25°C; CH₂Cl₂) and enthalpies ΔH° calculated according to Method 5 (see Section 2) for 1:1 adducts between di-iodine and benzazole-2-thione (**4**) and 2-selone (**5**) derivatives^a

	X	R	4		5	
			K (dm ³ mol ⁻¹) ^b	$-\Delta H^\circ$ (kJ mol ⁻¹) ^c	K (dm ³ mol ⁻¹) ^b	$-\Delta H^\circ$ (kJ mol ⁻¹) ^c
a	NH	H	4.57×10^3	33	—	—
b	NH	Me	1.08×10^4	43	8.61×10^5	51
c	NMe	Me	4.74×10^3	37	7.74×10^5	57
d	O	H	59.1	23	$8(1) \times 10^{3d}$	—
e	O	Me	57.0	25	3.21×10^3	31
f	S	H	5.67×10^2	37	—	—
g	S	Me	6.26×10^2	35	6.54×10^4	40

^a Data taken from [36].

^b Interpolated K values at 25°C are reported without standard deviations.

^c Estimated ΔH° values using the values reported at 17°C and 35°C.

^d $t = 17^\circ\text{C}$.

by ¹³C-NMR spectroscopy [13,47,59,60]. In fact, for the two series of compounds **6g–j** and **6a–d**, analogous trends were observed by following the ¹³C chemical shifts of solutions containing increasing amounts of I₂. Steric and electronic effects

Table 4

Formation constants K (25°C; CH₂Cl₂) and enthalpies ΔH° for 1:1 adducts between di-iodine and hydantoin derivatives (**6**)

	X	Y	R ₁	R ₂	K (dm ³ mol ⁻¹) ^a	$-\Delta H^\circ$ (kJ mol ⁻¹) ^b	Method ^b	Ref.
6a	S	O	H	H	2.01×10^2	33	5	[58]
b	S	O	H	Me	1.72×10^2	31	6	[61]
c	S	O	Me	H	1.49×10^2	22	6	[61]
d	S	O	Me	Me	31(1)	27(1)	5	[59]
e	O	S	H	H	68.5	39	5	[58]
f	O	S	H	Me	11.9	21	6	[61]
g	S	S	H	H	1.43×10^2	30	5	[58]
h	S	S	H	Me	1.26×10^2	27	6	[61]
i	S	S	Me	H	$1.31(4) \times 10^2$	24.5(7)	5	[59]
j	S	S	Me	Me	19.1(2)	17.7(8)	5	[59]
k	S	SMe	H	—	$1.10(8) \times 10^4$	56.8(3)	5	[60]
l^c	SMe	S	H	—	$6.4(2) \times 10^2$	45.3(7)	5	[60]
m	Se	O	H	H	2.06×10^4	40	5	[58]
n	O	Se	H	H	1.0×10^3	35	5	[58]
o	Se	S	H	H	1.34×10^4	31	5	[58]
p	S	Se	H	H	4.75×10^2	21	5	[58]
q	Se	Se	H	H	5.85×10^3	20	5	[58]

^a Interpolated K values at 25°C are reported without standard deviation.

^b See Section 2.

^c For the compound having $x = y = \text{sMe}$, K and ΔH° values related to the 1:1 adduct formulation have also been determined in CH₂Cl₂ according to method 5 in Section 2: $K = 14.6(8)$ (25°C) dm³ mol⁻¹; $-\Delta H^\circ = 24.8(8)$ kJ mol⁻¹.

Table 5

Formation constants K (25°C) and enthalpies ΔH° , calculated according to Method 2 (Section 2), for 1:1 adducts between di-iodine and thioacetamide (**7**) and substituted thioureas (**8**)

	R ₁	R ₂	R ₃	R ₄	Solvent	K (dm ³ mol ⁻¹) ^a	$-\Delta H^\circ$ (kJ mol ⁻¹)	Ref.
7	–	–	–	–	CH ₂ Cl ₂	8.60×10^{3a}	34(7)	[25]
8a	H	H	H	H	CH ₂ Cl ₂	8.50×10^{3a}	40(4)	[25]
					CCl ₄	8.82×10^{3a}	–	[8]
b	Me	H	H	H	CHCl ₃	1.31×10^4	–	[57]
					CCl ₄	1.05×10^{4a}	–	[8]
c	Me	H	H	Me	CHCl ₃	1.50×10^4	–	[57]
d	Et	H	H	Et	CHCl ₃	1.55×10^4	60	[57]
e	<i>i</i> -Pr	H	H	<i>i</i> -Pr	CHCl ₃	1.64×10^4	47	[57]
f	<i>t</i> -Bu	H	H	<i>t</i> -Bu	CHCl ₃	4.09×10^4	78	[57]
g	Me	H	H	<i>i</i> -Pr	CHCl ₃	1.71×10^4	–	[57]
h	Me	H	H	<i>t</i> -Bu	CHCl ₃	2.08×10^4	–	[57]
i	Me	H	H	Bz	CHCl ₃	1.03×10^4	–	[57]
j	Me	Me	Me	Me	CHCl ₃	1.36×10^4	40	[57]
					CH ₂ Cl ₂	$4.9(5) \times 10^{4a}$	38(7)	[26]
					<i>n</i> -C ₇ H ₁₆	$1.31(1) \times 10^{4a}$	41(5)	[26]
					CCl ₄	$8.0(2) \times 10^3$	44(2)	[26]
k	Ph	Ph	H	H	CHCl ₃	$6.57(5) \times 10^3$	–	[57]
l	<i>p</i> -MePh	<i>p</i> -MePh	H	H	CHCl ₃	$1.16(4) \times 10^4$	29	[57]
m	<i>p</i> -BrPh	<i>p</i> -BrPh	H	H	CHCl ₃	$2.3(1) \times 10^3$	–	[57]
n	<i>p</i> -MeOPh	<i>p</i> -MeOPh	H	H	CHCl ₃	$1.40(3) \times 10^4$	–	[57]
o	1-imidazolyl		1-imidazolyl	976	CH ₂ Cl ₂	978	30.4	[62]
					32(4)	[62]		

^a t = 20°C.

as well as hydrogen-bonding interactions have been used to account for the different donor properties of the thioxo sulfur atom in compounds **6a–l** [61]. Table 5 reports the data for the adduct formation with thioacetamide (**7**) [25] and variously substituted thioureas (**8a–o**) [2,8,25,26,57,62]. The thermodynamic parameters of **8a–j** show a fairly linear correlation in terms of the Taft [63] aliphatic polar substituent constants σ^* , as well as those of **8k–n** in terms of the Hammett σ constants [57]. The solvent effect on thermodynamic parameters for tetramethylthiourea (**8j**) has been rationalized in terms of the importance of dipole–dipole, Van der Waals, and other non-specific interactions between solute and solvent molecules in Mulliken's CT theory [56]. In Table 6 the formation constants and the enthalpies for 1:1 adducts between di-iodine and some miscellaneous thiones (**9–12**) are reported. Compounds **9a–c** [3,35], which differ from thioureas in the substitution of one nitrogen with a sulfur atom, present K values of about two orders of magnitude lower. This effect is enhanced when the sulfur is substituted by an oxygen atom (**10**) [3]. Unexpectedly, compounds **11** [40,46,64] show much lower K values than compounds **3** [40,46,64]. The reported tris(*N,N*-disubstituted dithiocarbamates)chromium (**12a–c**) [35] show remarkably low values of

Table 6

Formation constants K (25°C) and enthalpies ΔH° for 1:1 adducts between di-iodine and miscellaneous thiones **9–12**^a

		Solvent	K (dm ³ mol ⁻¹)	$-\Delta H^\circ$ (kJ mol ⁻¹)	Method ^b	Ref.
9a	$R_1 = R_2 = \text{Et}^c$	CH ₂ Cl ₂	3.44×10^2	19.2(4)	5	[35]
		CCl ₄	$2.97(5) \times 10^{2d}$	—	2	[3]
b	$R_1 = R_2 = \text{Bz}$	CH ₂ Cl ₂	61.3	14.2(8)	5	[35]
c	$R_1-R_2 = \text{morpholine}$	CH ₂ Cl ₂	91.3	18.4(4)	5	[35]
10	Tolnaftate ^e	CCl ₄	55(1) ^d	—	2	[3]
11	$R_4\text{todit}^f$	—	—	—	—	—
a	$R = \text{Me}$	—	—	—	—	—
b	$R = \text{Et}$	CHCl ₃	5.98×10^2	18(2)	7	[40]
c	$R = \text{Bu}$	CHCl ₃	2.24×10^3	39(3)	7	[46]
d	$R = \text{Ph}$	CHCl ₃	3.71×10^2	16.3(8)	7	[64]
12	$[(R_1R_2\text{NCS}_2)_3\text{Cr}]$	—	—	—	—	—
a	$R_1 = R_2 = \text{Et}$	CH ₂ Cl ₂	37.0	9.2(4)	5	[35]
b	$R_1 = R_2 = \text{Bz}$	CH ₂ Cl ₂	41.0	7.9(4)	5	[35]
c	$R_1-R_2 = \text{morpholine}$	CH ₂ Cl ₂	22.4	8.8(4)	5	[35]

^a The K and ΔH° values for the 1:1 adduct formation have also been determined in CHCl₃ using method 7 in Section 2 for a series of dithiooxamides having general formula $R_2\text{NC(S)C(S)NR}_2$ [54]: K (25°C) = 5.01×10^2 , 5.60×10^2 , 1.15×10^2 dm³ mol⁻¹; $-\Delta H^\circ$ = 26.8(2), 25.5(4), 27.2(4) kJ mol⁻¹ for $R = \text{Me}$, Et and $R_2\text{N} = \text{morpholine}$, respectively.

^b See Section 2.

^c Tetraethylthiuram disulfide (disulfiram).

^d $t = 20^\circ\text{C}$.

^e Methyl(3-methylphenyl)carbamothioic acid *O*-2-naphthalenyl ester.

^f 4,5,6,7-tetrathiocino [1,2-b:3,4-b'] diimidazolyl-1,3,8,10-tetraalkyl-2,9-dithione. The values reported above refer to 1:1 adduct formation. The authors have recently re-investigated all compounds **11** on the basis of the formation of both 1:1 and 1:2 adducts using Method 8 in Section 2 [46]. The reported values of $-\Delta H^\circ$ for **11a**, **b**, **c** and **d** are respectively 30.5(4), 31.0(4), 35.6(4), 25.1(4) kJ mol⁻¹ for the 1:1, and 64.4(4), 70.3(4), 72.8(4), 57.3(4) kJ mol⁻¹ for the 1:2 adduct formations. For **11c**, the K value for the 1:2 adduct formation has also been calculated in CHCl₃ using method 7 in Section 2: $K = 2.34 \times 10^2$ dm³ mol⁻¹ [46].

the K s; the coordination to the metal via both sulfur atoms reduces their donor abilities towards I₂. As a matter of fact, their formation constants resemble those reported for sulfides (see later).

On the basis of the reviewed papers on thiones, some additional remarks should be made: (1) small variations in the charge density on the donor atom produce a remarkable change in K ; (2) as a consequence, the K values strongly depend on the chemical environment of the donor atom and spread over a very wide range [from 10^4 – 10^5 dm³ mol⁻¹ for several imidazolidine-2-thione (**1b–f**) and imidazoline-2-thione (**3**) derivatives to 10–20 dm³ mol⁻¹ found in **6f** and **6j**]; (3) for compounds **1a–1i** and **6a–6q**, in which entropic effects can be considered of the same order of magnitude, $\ln K$ values show a linear correlation with the binding energies of the lone pair of the thioxo sulfur atom, measured by UPS spectroscopy [61,65–67]; (4) for several thiones a correlation between the formation enthalpies and the $\nu(\text{I–I})$

stretching vibrations, measured by FT-Raman spectroscopy, has been reported [14,60]. The data are well-interpolated by a second-order polynomial equation and this correlation has been considered useful in evaluating the strength of the donor–I₂ interaction.

4. Selones

The studied selones **2**, **5**, **6** [36,58,65], which are less numerous than the thiones, are also reported in Fig. 1. Their formation constants and enthalpy values for equilibrium (1) are reported in Table 1 for compounds **2** [36,65], Table 3 for compounds **5** [36] and Table 4 for compounds **6m–6q** [58,68]. In agreement with the higher polarizability [7] of the selenium atom and with the better match between the energies of the Se lone pair and the σ^* orbital of di-iodine, selones give more stable adducts than the corresponding sulfur isologs. A comparison of *K* values within corresponding series of thiones and selones (compare, for example, **1** with **2** or **4** with **5**) shows that the X substituent in the ring has similar effects on the donor properties of the two exo-chalcogen atoms. One interesting point worth mentioning is that the data for selones fall in the same linear correlation between $\ln K$ vs. the ionization energies of the lone pair of the donor atoms reported for several thiones [61,65–67]. In the Se-containing hydantoin derivatives **6m–q** (Table 4), the higher *K* values compared with those of **6a–j** indicate the selenium as the donor atom, confirming that the CT-interaction becomes stronger according to the order O < S < Se. The *K* values of **6o/6p** show the same trend as for the couple **6a/6e**, as regards the position of the chalcogen donor atom in the hydantoin skeleton [58]. A good correlation between the $\ln K$ values vs. the charge density (calculated using the PM3 semi-empirical method) of the donor atom has been reported for several hydantoin derivatives (**6a**, **6e**, **6g**, **6l**, **6m**, **6o**, **6p** and **6q**) [58].

5. Sulfides

Several classes of acyclic R₁–S–R₂ (**13**) [69–73], cyclic [n]aneS_m (**14–19**; *n* represents the total number of atoms of the ring and *m* the number of sulfur atoms) [14,45,49,74–76] and heterocyclic (**20–27**; Fig. 1) [8,29,77] sulfides have been considered in the reaction with di-iodine. Their formation constants at 25°C together with ΔH° values for 1:1 molecular adducts with I₂ are reported in Tables 7–11. On the whole, sulfides show formation constants of several orders of magnitude lower than those observed for thiones; however, as for thiones, they are sensitive to the chemical surroundings of the donor atom. In particular, for the acyclic R₁–S–R₂ sulfides (**13**; Table 7), in the case of only alkyl substituents (**13a–e**, **m**) [69–71], the *K* values are very similar and are only slightly dependent on the +I effect of the alkyl groups [69]. When at least one of the substituents is a phenyl or a substituted phenyl group (**13f–l**, **n**), the *K* values are remarkably lower [71,72].

Table 7

Formation constants K (25°C) and enthalpies ΔH° for 1:1 adducts between di-iodine and several R_1-S-R_2 acyclic sulfides (**13**)

	R_1	R_2	Solvent	K (dm ³ mol ⁻¹)	$-\Delta H^\circ$ (kJ mol ⁻¹)	Method ^a	Ref.
13a	Me	Me	CCl ₄	74.0(5) ^b	34.7(4)	2	[69]
b	Me	Et	CCl ₄	107.0(5)	30.5(4)	2	[69]
c	Me	<i>n</i> Pr	CCl ₄	112.0(8)	34.3(8)	2	[69]
d	Me	<i>n</i> Bu	CCl ₄	115.0(4)	32.2(8)	2	[69]
e	Me	<i>n</i> De	CCl ₄	120(1)	32(1)	2	[69]
f	Me	Ph	C ₆ H ₁₂	12.1	23.0	1	[71]
g	Me	<i>p</i> -FPh	C ₆ H ₁₂	8.9	27.2	1	[71]
h	Me	<i>m</i> -FPh	C ₆ H ₁₂	4.3	22.1	1	[71]
i	Me	<i>p</i> -ClPh	C ₆ H ₁₂	5.6	24.2	1	[71]
j	Me	<i>m</i> -ClPh	C ₆ H ₁₂	4.6	24.2	1	[71]
k	Me	<i>p</i> -BrPh	C ₆ H ₁₂	5.9	24.2	1	[71]
l	Me	<i>p</i> -MePh	C ₆ H ₁₂	19.6	26.3	1	[71]
m	Et	Et	<i>n</i> C ₇ H ₁₆	187(3) ^b	32.6	1	[70,73]
n	Ph	Ph	C ₆ H ₁₂	3.9	23.8	3	[72]
o	H	Et	C ₆ H ₁₂	23.2	19.2	3	[72]
p	H	Ph	C ₆ H ₁₂	11.6	18.0	3	[72]

^a See Section 2.

^b Calculated by NMR spectroscopy (Method 9 in Section 2) in CCl₄ at 25°C: 71(5) dm³ mol⁻¹ for **13a** and 171(23) dm³ mol⁻¹ for **13m** [73].

The same effect is observed when one alkyl group is substituted by a hydrogen atom (**13o**, **p**) [72]. Table 8 sums up the results obtained for cyclic sulfides (**14–19**) belonging to the general class $[n]\text{aneS}_m$ [14,45,49,62,74–76]. Although most cyclic sulfides have two or more sulfur atoms potentially capable of binding di-iodine to form adducts higher than 1:1, the presence of isosbestic points as well as the results of Job's method indicate that only 1:1 adducts are formed [14,45,49,76,78]. An inspection of Table 8 reveals that for rings of the same size, the values of K decrease as the number of S-donors increases (**14c/15/16/17**). Otherwise, in the presence of the same number of sulfur atoms, K increases on increasing the size of the ring (see, for example, **14a/b/c** and **18b/19a/19b**). These trends have been explained in terms of the inductive effect of the sulfur atoms ($-I$), or vice versa in terms of the $+I$ effect of the methylene groups [14]. A rough linear correlation has been reported between the $\ln K$ and the number of CH₂ per sulfur atom, which has been considered a convenient parameter to measure both inductive effects of the atoms in the cyclic sulfides [14]. For this series of compounds, the $\nu(I-I)$ Raman frequencies have been correlated [14] with the measured formation enthalpies, but these data do not fit the same correlation found for thiones. The slight difference in two correlations has been ascribed to the different hybridization of the sulfur atom in the two sets of compounds.

Several heterocyclic sulfides (**20–27**) have also been studied [8,29,77] in the reaction with di-iodine, and the formation constants and enthalpies are reported in Tables 9–11. Many of them have been studied because of their strong antithyroid

Table 8

Formation constants K (25°C; CH₂Cl₂) and enthalpies ΔH° for 1:1 adducts between di-iodine and cyclic sulfides [n]aneS_m (**14–19**)

	<i>n</i>	<i>m</i>	<i>p</i>	K (dm ³ mol ^{−1})	$-\Delta H^\circ$ (kJ mol ^{−1}) ^a	Method ^b	Ref.
14a	4	1	1	79(3) ^{c,d}	29.4(7)	3	[74]
b	5	1	2	182 ^{c,d}	36.4(1.7)	3	[75]
c	6	1	3	827(26)	47.2(1)	6	([14]a)
				135 ^{c,d}	29.7(1.3)	3	
15	6(1,3)	2	–	94(3)	32.3(3)	6	([14]a)
16	6(1,4)	2	–	40(1)	31.8(1)	6	([14]a)
				77 ^c	25.9(1.3)	2	
17	6	3	–	13(1) ^d	26.4(1)	6	[49]
				7 ^c	19.2(1.7)	2	[75]
				31(2)	20.8(3)	1,2	[76]
18a	9	3	1	169(4)	35.0(1)	6	[45]
b	12	4	2	74(7)	28.3(2)	6	([14]a)
c	15	5	3	94(1)	29.8(1)	6	([14]a)
d	18	6	4	151(2)	31.6(1)	6	([14]a)
e	24	8	6	213(5)	33.6(1)	6	([14]b)
19a	14	4	1	151(4)	32.2(1)	6	([14]a)
b	16	4	2	519(9)	38.7(1)	6	([14]a)

^a Formation enthalpies have been calculated from $\ln(Kx)$ vs. $1/T$ (see Section 2) [14a,b].

^b See Section 2.

^c CCl₄ solution.

^d For these compounds the K values have also been calculated by NMR spectroscopy according to the Method 9 in Section 2 (CCl₄; 25°C): 96(11) for **14a**, 216(17) for **14b** and 136(30) dm³ mol^{−1} for **14c** [73]; 12.8(1) dm³ mol^{−1} for **17** (CH₂Cl₂; 25°C) [49].

activity [8]. A comparison of the K values of **20a–d** [29] with those of **21** [29] and **22** [8] shows that they increase remarkably as the donor molecules become less aromatic (Table 9). The same effect is observed on comparing compounds **23a–b** with **24a–f** (Table 10) [77]. Compounds **25–27** with a strong antithyroid activity in rats also have relatively high K values (Table 11) [8].

Table 9

Formation constants K (25°C) and enthalpies ΔH° , calculated using Method 2 (see Section 2), for 1:1 adducts between di-iodine and miscellaneous heterocyclic sulfides containing the thioether group (**20–22**)

	R ₁	R ₂	R ₃	Solvent	K (dm ³ mol ^{−1})	$-\Delta H^\circ$ (kJ mol ^{−1})	Ref.
20a	H	H	H	CCl ₄	9(1)	22.5(7)	[29]
b	Me	H	H	CCl ₄	17(1)	28.5(6)	[29]
c	Me	ClC ₂ H ₄	H	CCl ₄	20(1)	29.6(6)	[29]
d	Me	ClC ₃ H ₆	H	CCl ₄	25(1)	27.9(7)	[29]
21	–	–	–	CCl ₄	1200(86) ^a	–	[29]
22	–	–	–	CCl ₄ /CHCl ₃	841(17) ^a	–	[8]

^a $t = 20^\circ\text{C}$.

Table 10

Formation constants K (20°C; CCl₄), calculated using Method 2 (see Section 2), for 1:1 adducts between di-iodine and thiazolinylnpyridyl sulfides (**23**) and thiazolinylnpyrimidinyl sulfides (**24**)^a

	X	Y	R ₁	R ₂	S-T ^b	K (dm ³ mol ⁻¹)
23a	CH	CH	H	H	2	21
b	CH	CH	H	H	3	31
24a	CH	CH	H	H	2	356
b	CH	CH	NO ₂ (3)	H	2	403
c	CH	CH	NO ₂ (5)	H	2	433
d	CH	CH	NO ₂ (3)	NO ₂ (5)	2	187
e	N	CH	H	H	2	795
f	CH	CH	OH (3)	H	2	1493

^a Data taken from [77].

^b This number indicates the position on the pyridyl (or pyrimidinyl) ring to which the sulfur atom is bound.

6. Selenides

Compared with sulfides, fewer selenides have been studied, and the obtained results are shown in Tables 12 and 13 for the acyclic (**28**) [79,80] and cyclic selenides (**29–30**) [49,78], respectively. As expected, the K values are generally higher than those measured for the sulfur isologs. The only cyclic selenides for which the formation constants have been determined in the reaction with di-iodine, are compounds **29a–c** (Table 13) [78]. [6]aneSe₃ (**30**) has also been studied in this respect [49], but because of its low solubility, the formation constant for the 1:1 adduct with I₂ has not been reported. However, a Job's plot shows that also in this case, as in the case of cyclic thioethers with several sulfur atoms, only the 1:1 adduct is formed [81].

Table 11

Formation constants K (20°C; CCl₄), calculated using Method 2 (see Section 2), for 1:1 adducts between di-iodine and miscellaneous polycyclic sulfides (**25–27**)^a

	R ₁	R ₂	K (dm ³ mol ⁻¹)
25a	Cl	(CH ₂) ₃ N(C ₂ H ₅) ₂	2507
b	Cl	(CH ₂) ₃ N(CH ₃) ₂	3168
c	H	CH ₂ CH(CH ₃)N(CH ₃) ₂	4259 ^b
26	H	CH ₂ CH(CH ₃)N(CH ₃) ₂	2683
27	Cl	CH(CH ₂) ₂ N(CH ₃) ₂	3401

^a Data taken from [8].

^b $t = 17^\circ\text{C}$.

Table 12

Formation constants K (25°C; CCl₄) and enthalpies ΔH° , calculated using Method 2 (see Section 2), for 1:1 adducts between di-iodine and several R–Se–R selenides (**28**)

	R	K (dm ³ mol ^{−1})	$-\Delta H^\circ$ (kJ mol ^{−1})	Ref.
28a	Me	472(50)	35.9	[79]
b	Ph	28.0	–	[79]
c	<i>p</i> -MeOPh	52.6	31.8	[80]
d	<i>p</i> -EtOPh	76.9	–	[80]
e	<i>p</i> -MePh	40.0	28.8	[80]
f	<i>o</i> -MePh	5.6	–	[80]
g	<i>p</i> -ClPh	8.3	17.6	[80]
h	<i>o</i> -ClPh	4.6	–	[80]

7. Conclusions

Different substrates containing sulfur and selenium donor atoms have been reviewed as donors for the formation of 1:1 CT-adducts with di-iodine. Although the methods of calculation that have been used to determine the formation constants and the ΔH° values are numerous and diverse, the following general conclusions can be drawn:

1. Se-based donors bind di-iodine more strongly than the corresponding sulfur isologs;
2. Thiones and selones generally bind di-iodine more strongly than sulfides and selenides;
3. The calculated K values spread over a very wide range of values depending on the chemical surroundings of the donor atom; they are strongly affected by even small changes in the charge density of the donor atom. Consequently, in compounds containing the framework R₁–C(=X)–R₂ (X = S, Se), the K values decrease according to the following sequence of R₁ and R₂: NR ≥ alkyl > aromatic > S > O;
4. When the donor atom is part of an aromatic system, the K values are generally lower than in the corresponding non-aromatic molecules;

Table 13

Formation constants K (25°C; CCl₄) and enthalpies ΔH° , calculated using Method 2 (see Section 2), for 1:1 adducts between di-iodine and cyclic selenides (**29–30**)

		K (dm ³ mol ^{−1})	$-\Delta H^\circ$ (kJ mol ^{−1})	Ref.
29a	[6]aneOSe	138	31.8	[78]
b	[6]aneSSe	198	30.9	[78]
c	[6]aneSe ₂	282	29.3	[78]
30^a	[6]aneSe ₃	–	–	[49]

^a K and ΔH° could not be calculated due to the low solubility of **30**.

5. For both sulfides and selones, the two correlations between the $\nu(\text{I-I})$ Raman stretching frequencies and the ΔH° values allow an evaluation of the formation enthalpies on the grounds of the $\nu(\text{I-I})$ stretching frequencies. This is very useful whenever the determination of the K values is prevented by experimental difficulties.

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